# The Interrelationship between Thermodynamics and Energetics: The True Sense of Equilibrium Thermodynamics

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*Es ist doch sonderbar bestellt,*
*Sprach Hänschen Schlau zu Vetter Fritzen,*
*Dass nur die Reichen dieser Welt*
*Das meiste Geld besitzen.*

*Gotthold Ephraim Lessing (1729-1781)*

*It's truly weird as if on cue,*
*Told Hansi Smart to cousin Funny,*
*That only rich men feed anew,*
*While beggars breed the money*
*As cited by Prof. Dr. Ernst Mach during his lecture about*
*the energy conservation law – on 15. Nov. 1871*

**Abstract:** The interrelationship between the conventional thermodynamics and energetics has been discussed in detail. A number of flavors has been considered in the field of energetics, with the conclusion that the actual difference among all of them is rather superficial. A need to reconsider the foundations of thermodynamics and statistical physics has been pointed out. Such a re-consideration ought to facilitate formulating thermodynamics at any level of matter organization: from the microscopic through nano- and mesoscopic to the macroscopic one.

**Keywords:** Thermodynamics, Energetics, Enthalpy, Entropy, Statistical Mechanics.

## INTRODUCTION

Energetics is very well known to be a generally significant branch of knowledge dealing with the modalities of all the possible energy conversions in all the available diversity of real and actual processes in our Universe. Therefore, one might speak of one of the truly general standpoints in this case [1-12].

Still, it is not completely clear for the present, how to combine the field of energetics with the conventional scope of thermodynamics – that is, the so-called "equilibrium thermodynamics" – although at the first glance the central topic of these both fields consists in properly dealing with the energy conservation and conversions...

Still, the scientific research is meanwhile following its further promising directions, just as it ought to, whereas one of the hottest topics nowadays is represented by the nanoscience. Consequently, marvelous and truly stimulating books are being published in the field (cf., for example [13-15] which represent a unique set entitled: "Lessons from Nanoscience: A Lecture Note Series").

The idea behind this series of books, as clearly formulated by one of its senior editors, sounds as follows:

(1)     It introduces the seminal concepts of nanoelectronics and mesoscopic physics.

(2)     And it shows that these concepts are not only relevant to small conductors but can also be used to obtain many standard results in the transport theory of large conductors in a relatively straightforward way.

This second point represents the *new perspective* and both (1) and (2) could be of broad relevance to the general problems of non-equilibrium statistical mechanics involving the emergence of irreversibility from reversible laws.

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With this in mind, the authors claim to have tried making the key concepts accessible to a broad audience.

In reading the books attentively, one can immediately recognize that the authors' aim has definitely been achieved to about 90% – the students and newcomers to the field ought to get the most of the necessary information.

The following points are, meanwhile, still remaining without a detailed consideration in these books:

(A)    When successfully using the "standard results in the transport theory of large conductors" at the nano- and mesoscopic levels of consideration – there is a non-negligible risk of being excessively attracted by superficial mathematical parallels (the examples are very well known, described and analyzed [16]). Well, such an aspect of the story in question shouldn't be a significant bother to anybody, if the nanoscience would solely be an enthralling form of spending our leisure time. But we are busy with working out a basis for future nanotechnologies… This is why, the mathematics, in effect, ought to be nothing more than our reliable toolset to reveal and check the actual working physical-chemical-… etc. principles.

(B)    The latter preoccupation arises especially when the reader of the books [13-15] is confronted with the degree of prestidigitation the authors show in dealing with the terminology like "equilibrium", "non-equilibrium", "reversible", "irreversible"... The prestidigitation of such a kind is also very long known – and had already received its fully deserved and to 100% proper estimate [8, 17].

With all this in mind, we have already triggered a discussion as to the fundamental principles of thermodynamics [18]. And the present communication represents its continuation.

**MIGHT THE CONCEPTUAL FRAMEWORK OF ENERGETICS BE OF USE IN THERMODYNAMICS?**

The first colleague who posed this question was Prof. Dr. Georg Ferdinand Helm (1851-1923). He started systematically working on energetics already during his initial employment as a grammar school lecturer (just in the school he had graduated himself: *Annenschule, Dresden* in Germany) – and was continuing his studies after being awarded a

professorship at the Technical University (that time: *Technische Hochschule*) of Dresden, Germany. He was a serious specialist in mathematics and theoretical physics, and this can immediately be followed in the list of his publications [1, 19-24].

The following was a very important point, as concerns the contribution of Prof. Dr. Helm: He had not just solely coined the term "mathematical chemistry", but was intensively working at foundations of such a discipline. This had fortunately been recognized already during his life-time, so that his book on the subject, published originally in German [21], had been translated and published in English [22] – to be spread among the colleagues in the Great Britain and USA.

Of lively interest to our present discussion is Prof. Dr. Helm's statement he placed in the Preface to his books [21, 22], namely:

*"The title "Mathematical Chemistry" means that the purpose of this little book is to collect the results, according to the deductive method, of the investigations in the realm of general chemistry.*

*The subject of the mathematical consideration of nature, which in its earlier development was known as Physical Chemistry, can now, in its present state, be viewed from a general theoretical standpoint as a whole: and in this state it appears as one of the clearest and most complete proofs of the principle of the conservation of energy. The fact that single parts of mathematical chemistry are derived from other reasoning, without regard to, or with mere passing consideration of, this general principle – as, e. g., the conception of the Osmotic Pressure from the analogy to gases, or from hypothetical molecular theories – can be attributed to the difference in the points of departure of these investigations, and also to the earlier lack of recognition of the Theory of Gibbs."*

Prof. Dr. Helm had raised here two important points.

(1)    The starting point for any kind of constructive consideration of natural phenomena is the principle of *conservation* (and – we dare to add here – *transformation*) of energy. And here is nothing to demur. But, remarkably, at the same time Prof. Dr. Helm was clearly slighting here the standpoints based upon "*analogy to gases*" and "*hypothetical molecular theories*". This demonstrates his belonging to the (at their days) powerful cohort of the so-called "Anti-atomists", like the outstanding chemist and natural

philosopher Prof. Dr. Wilhelm Ostwald (1853-1932) [25, 26], as well as the outstanding physicist and philosopher Prof. Dr. Ernst Mach (1838-1916) [27, 28], prominent anti-atomist chemists and philosophers like Pierre Berthelot (1827-1907), Henri Le Chatelier (1850-1936), Pierre Duhem (1861-1916) and František Wald (1861-1930) – among many other serious specialists …

Well, now we know very well that "the Anti-atomists" were successfully defeated by the "Atomists", whereas among the latter were such outstanding specialists as Prof. Dr. Ludwig Boltzmann (1844-1906) and Prof. Dr. Max Planck (1858-1947). Interestingly, the latter story still doesn't seem to come to its natural end even nowadays. Indeed, in the most recent, very interesting and very stimulating report by Klaus Ruthenberg [29] we read:

*"During the 19-th century, atomism became a central model in the chemical sciences. However, the particular sort of atomism which is sometimes called "chemical atomism" was by no means founded on convincing empirical data, and developed no significant explanatory power. In fact, it has been a metaphysical concept, a heuristic speculation, put forward with a view to explaining certain law-like statements of general or theoretical chemistry. Among these law-like statements were the basic stoichiometric principles of chemistry (e. g., the proportion laws). Atoms were postulated as tiny material balls with purely mechanical functions. Later, ad-hoc attempts to attach additional properties to the atom concept where made. Only with the rise of quantum mechanics and quantum chemistry in the third decade of the 20-th century did the atomistic picture change dramatically, departing entirely from the classical realist interpretation of small particles, although most chemists kept and still cling to their traditional "naive-realistic" – some may prefer "pragmatic" – attitude."*

In effect, both atomists and anti-atomists are not completely wrong. And the important points ought to be as follows. First of all, the conventional traditional "equilibrium" thermodynamics is logically incomplete and should be reworked in detail (we have already discussed this at more length elsewhere [18]). Secondly, the conventional statistical mechanics embodying the atomistic representation is possessed of a rather fuzzy basement: In trying to deal with the "large number of atoms/molecules" we are immediately jumping into the well-known SORITES paradox [18].

With all this in mind, to reconcile the above-mentioned "pragmatic-vs.-atomistic" conceptual gap, first we ought to take into account that the First and the Second Basic Laws of thermodynamics are not independent from each other. In fact, they both do belong to one and the same law, and represent just the two opposite faces of the latter (something like "Janus Bifrons" or "Yin-Yang" mascots) [18]. And such a unique law physically ought to work at every possible level of consideration, that is, from the true microscopic – through the nano- and mesoscopic – to the true macroscopic ones.

Secondly, the statistical mechanics ought to be reformulated by taking into account the intrinsic fuzziness of the problem – one of the possible skillful ways to achieve such a goal seems to be the Bayesian statistics [18].

(2)   The theories of Prof. Dr. Josiah Willard Gibbs (1839-1903) are indeed absolutely indispensable on our way to build up the true physical chemistry/chemical physics. We would like to discuss here in detail the efforts to systematically comprehend and employ them. In this respect, it is also important to attentively consider everything what is anyway connected with the legacy of Prof. Dr. Pierre Duhem.

## JOSIAH WILLARD GIBBS, HIS IDEAS AND THEIR FURTHER DEVELOPMENT; THE WORK AND IDEAS OF AUGUST FRIEDRICH HORSTMANN

Prof. Dr. Gibbs himself, his life and work surely don't need any additional introduction [30, 31]. Still, of particular interest for our present discussion is the fact just mentioned above, namely that although Prof. Dr. Gibbs was definitely sharing the atomistic standpoint (especially his last publication, cf. [31], proves such a statement) the anti-atomists had nonetheless recognized his results. Not only the consequent energetist and anti-atomist Prof. Dr. Helm expressed his sincere respect toward Prof. Gibbs' work, but also the eminent chemist, consequent energetist and anti-atomist Prof. Dr. Pierre Duhem had also paid very serious attention to Gibbs' results [32] (later on we will discuss here Prof. Duhem's considerations in detail). The reason for such an effect lies most probably in that Prof. Gibbs was systematically following the *both* (seemingly) antagonist directions of thought – the atomistic and the energetic one … We use here the word 'seemingly' because the antagonism between the both is in effect purely anthropomorphic and – therefore

– imaginary … But Prof. Gibbs had, to our sincere regret, not enough time upon Earth to successfully and convincingly demonstrate this clear point …

With all this in mind, it would be of definite interest to consider how the 'energetic' ideas of Gibbs were developed after his departure. One of the well known first stations for this train of thoughts was the work by Prof. Dr. Joseph H. Keenan who had performed a thorough logical analysis of all the modern (at his time) achievements in the field of thermodynamics using the Gibbs' approach (cf. [33] and the references over there).

Of interest and importance for our present discussion is the notion of '*availability*' clearly formulated by Prof. Keenan (and originally introduced by Prof. Gibbs).

The 'availability' is the logical result of simple and rigorous consideration of the First and the Second Laws of thermodynamics. Prof. Keenan had stated the First Law in terms of 'work' and 'heat' alone, and *only then* he rigorously and quantitatively defined the term 'energy'. He was *intentionally avoiding the employment molecular/atomic picture*, for the physical sense of the latter holds only for idealized gases, but he was nonetheless capable of convincingly demonstrating, what kind of property is represented by the notion of 'internal energy' (**sic!**).

A great achievement of Prof. Keenan was to rectify the statement of the Second Law into a single valid statement – and to derive all the logically possible equivalents thereof just as corollaries. With this in mind, Prof. Keenan had analyzed in full detail the notion of 'entropy' and the results of Clausius.

As a result of all the above-mentioned considerations, Prof. Keenan was capable of introducing the notion of 'availability' as [33]:

*"the maximum work which can result from interaction of system and medium when only cyclic changes occur in external things except for the rise of a weight".*

He had herewith restricted the whole consideration to the Carnot-like models only and proven that the amount of the 'availability' thus defined might quantitatively be expressed using the Gibbs' potential (also known as '*Gibbs free energy*' and '*free enthalpy*' with the first of the both having the clear physical sense and the second one being definitely a misnomer of the

kind consistently criticized in [17]). Indeed, in introducing the latter function, Prof. Gibbs himself had explained the problem and its solution as follows [34]:

*"For example, let it be required to find the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition. This has been called the **available energy** of the body. The initial state of the body is supposed to be such that the body can be made to pass from it to states of dissipated energy by reversible processes."*

A propos, denoting the Gibbs function as 'free enthalpy' is quite widespread and defended in the work [35] as a method to underline the difference between the "Gibbs' free energy" and the "Helmholtz' free energy". In effect, this is nothing more than a pure semantic prestidigitation bearing no clear physical sense. We have already considered the intrinsic interconnection between the pertinent Gibbs' and the Helmholtz' functions [18], so bearing this in mind we shall discuss here in detail the physical sense of these functions and their hierarchy within the Gibbs-Keenan 'availability' concept.

But, first of all, there is one important point to be stressed here: The Gibbs' function being a *free, available energy* on the one hand and a *potential* (energy) on the other ought to connect the Gibbs-Keenan's concept of 'energy availability' with the feasibility of some equilibrium state. Both Gibbs and Keenan were discussing in detail the possible equilibrium states (stable, unstable, neutral). Still, the both colleagues were remaining within the Carnot-like reversible (cyclic) models… Nonetheless, they both were very-very close to grasp the true validity of Carnot's ingenious model… What had prevented them from going this last decisive step? Most probably, the actual reason was the incomplete treatment of Clausius' legacy…

Was Clausius' legacy indeed so difficult to grasp? No, of course not! The reason is that the information about Clausius' results and their proper interpretation were at Gibbs', as well as at Keenan's time by far incomplete. These reasons are completely objective, for nobody could/can be accused of anything – and we have already discussed the situation in part [18]. The keys to the final explanation of the situation at hand

could be found in the works of Prof. Dr. Pierre Duhem, who was a propos one of the powerful energetists and fierce anti-atomists…

In one of his marvellous books [32] dedicated to the 'thermodynamic potential', Prof. Dr. Duhem analyzed in detail the works of Gibbs and of one of colleagues whose name isn't widely known and recognized – namely, Prof. Dr. August Friedrich Horstmann. Regretfully, the text of Prof. Duhem's citation isn't revealing enough, but, fortunately, he presented the reference to the original work by Prof. Horstmann.

It would definitely be of help to present here a short note introducing Prof. Horstmann (1842-1929). He was a fine specialist in the field of physical chemistry, especially in the area of chemical thermodynamics. He was a student of Rudolf Clausius, so that he was eager to embody the authentic ideas of his teacher in applying the Second Law of thermodynamics to study chemical equilibria. He published his works on this theme in German scientific journals at about the same time as Gibbs published his works in the USA media. Meanwhile, to our sincere regret, Prof. Horstmann had serious problems with his eye-sight since his childhood – and lost his eye-sight completely by 1902. This is why; he had practically no possibility to promote his professional achievements, although, nonetheless, he might undoubtedly be considered one of the actual founders of the Chemical Thermodynamics.

And now let us consider the actual achievements of Prof. Horstmann in the chemical thermodynamics. At the time of his full activity he published a number of very important papers and participated in editing a handbook [36-39], but still his name remains to be not widely known and recognized.

Prof. Horstmann's view of the Second Basic Law is of especial significance for our present discussion, so that we shall present it here in detail. In particular, Prof. Horstmann communicates [36]:

*"Die Formel $\delta Q = AT \dfrac{dp}{dT} \delta V$ ergibt sich, wie Jeder weiß, der mit der mechanischen Wärmetheorie vertraut ist, unmittelbar aus dem zweiten Hauptsatz $\left( \int \dfrac{dQ}{T} = 0 \right)$ unter der einzigen Voraussetzung, dass der Energieinhalt eines Körpers während der betrachteten Änderung des Zustands durch Volumen und Temperatur eindeutig bestimmt sei. Sie gibt dann die Wärmemenge, welche bei jener Änderung, gleichgültig wozu, verbraucht wird.*

*Jene Voraussetzung ist in den behandelten Fallen erfüllt. Denn wenn man z. B. eine Gewichtseinheit Salmiak von einem gegebenen Anfangszustand auf ein bestimmtes Volumen und eine bestimmte Temperatur bringt, so ist ein bestimmter Teil verdampft und man muss eine bestimmte Wärmemenge zuführen.*

*Somit gilt hier jene Formel, so gut wie der Hauptsatz selbst. Da ferner bei dem Beweis den Letzteren bekanntlich keinerlei Annahmen über die Molekularkonstitution der Körper und die Änderung derselben bei thermischen Vorgängen, oder über die Art der Wärmebewegung gemacht werden, so ist auch jede strenge Folgerung an demselben vollständig unabhängig von dem Wert unserer Hypothesen über die molekularen Vorgänge. Bei dem Schmelzen des Eises z. B. sind wir in dieser Beziehung noch heute völlig im Dunkeln, und doch hat die obige Formel schon vor 20 Jahren die Erniedrigung des Schmelzpunktes durch erhöhten Druck richtig vorausgesagt."*

*"The formula $\delta Q = AT \dfrac{dp}{dT} \delta V$ can be directly derived from the expression for the Second Law $\left( \int \dfrac{dQ}{T} = 0 \right)$, as known to everybody who is acquainted with the mechanical theory of heat, bearing in mind the only assumption that the energy content of a body during its state change under study can be determined without any ambiguity through nothing more than the volume and temperature. The formula describes then the heat quantity which is consumed during the change in question, irrespective of what are the way and the sense of this consumption.*

*Such an assumption is safe in the cases we discuss here. Because, if we bring, say, a definite amount of ammonium muriate from its given initial state to some definite volume and some definite temperature, then some definite amount of heat will be added to the stuff and hence the definite amount of the latter will evaporate.*

*This is why, both the formula discussed above and that for the Second Law itself are fully applicable here. Moreover, it is well known that if during the proof of the latter no assumptions are made as for the molecular construction together with its possible change during thermal processes, or as to the particular sort of the thermal motion, then the pertinent conclusion will anyway be independent of the validity of our assumptions concerning the molecular processes as well. For example, we are still in the dark as concerns the molecular processes during the ice melting, but the*

*formula we discussed above is already since 20 years working correct when predicting the increase of the melting point as a result of an increase in pressure."*

This remark by Prof. Horstmann is of clear and crucial methodological importance for correct and relevant dealing with the Second Law of thermodynamics – which is valid both at the macroscopic and at the microscopic level of consideration.

And another remark by Prof. Horstmann, which is of extreme importance for our present discussion, because it is clearly explaining the very intrinsic sense of the Second Law, is sounding as follows (Remarkably, below we'll show only the methodological introduction, whereas what follows is a clear pointer to a peaceful reconciliation of all the ancient struggles between the energetists and atomists, as concerns the true role of the statistical physics in chemistry [37], but the details of the latter part are far beyond our scope here):

*"Gewisse Zersetzungserscheinungen, welche in letzterer Zeit ausführlicher studiert worden sind, gestatten zum ersten Male eine Anwendung des zweiten Hauptsatzes der mechanischen Wärmetheorie in Füllen, wo die Wärme chemische Verbindungen nach festen Verhältnissen zerlegt, wo sie Arbeit leistet gegen die Kraft, die man chemische Verwandtschaft nennt. Es zeigt sich damit, worauf schon öfter hingewiesen worden, dass auch für den Chemiker die Lehren, welche die Wärmetheorie in jenem Satz zusammengefasst hat, von hohem Interesse sind. Wenn trotzdem diese Lehren nur dem Physiker bekannt sind, so liegt dies daran, dass eine strenge Ableitung derselben nur durch ziemlich abstrakte mathematische Betrachtungen möglich und eine wirklich populäre Darstellung noch nicht versucht ist. Ich schicke der Anwendung, die ich zu machen beabsichtige, eine Darlegung der betreffenden Resultate der Wärmetheorie voraus, welche vielleicht zu deren Popularisierung beitragen kann. Es macht diese Darstellung weder auf Originalität noch auf Strenge Anspruch; sie soll weiter nichts, als mit Hilfe bekannter Hypothesen in möglichst elementarer Weise die Bedeutung der betreffenden Gleichungen versinnlichen.*

1.   *Wärme kann in Arbeit verwandelt und Wärme aus Bewegung erzeugt werden. Wir schließen daraus, dass Wärme selbst eine Bewegung sei; denn auch Bewegung kann in Arbeit umgesetzt*

*werden. Die Quantität der Arbeit welche entstehen kann, ist gleich der lebendigen Kraft der Bewegung, d. h. dem halben Produkt aus dem Quadrat der Geschwindigkeit in die Masse des bewegten Körpers. Das Gleiche gilt für die Wärme; eine gegebene Quantität Wärme repräsentiert eine bestimmte Menge lebendiger Kraft, die gleich ist der Arbeit, welche aus der Wärmemenge erzeugt werden kann. Dies ist der durch die Erfahrung bestätigte Inhalt des ersten Hauptsatzes der mechanischen Wärmetheorie: Arbeit und Wärme sind äquivalent.*

2.   *Es lehrt nun aber die Erfahrung, dass nicht jede beliebige Wärmemenge sich, ohne Weiteres in Arbeit umsetzen lässt, und der Umstand, dass in den kalorischen Maschinen immer Wärme von höherer Temperatur angewendet wird, weist darauf hin, dass die Temperatur bestimmt, wie viel von einer gegebenen Wärmemenge in Arbeit verwandelt werden kann. Dies bestätigt sich, wenn man beachtet, dass die Erzeugung von Arbeit aus Wärme immer dadurch geschieht, dass ein Körper sich unter dem Einfluss der Wärme ausdehnt und bei dieser Ausdehnung Widerstände überwindet; diese Widerstände aber, welche bei der Ausdehnung überwunden werden können, bei der Anwendung verschiedener Körper sehr verschieden, sind bei demselben Körper um so größer, je höher die Temperatur ist. was namentlich bei Gasen und Dämpfen deutlich hervortritt. Die Arbeit, welche die Wärme bei solchen Vorgängen leisten kann, wächst demnach mit der Temperatur; das Gesetz, nach welchem, dieses Wachsen stattfindet, lässt sich jedoch nicht aus der direkten Beobachtung ableiten, weil im Allgemeinen nicht nur gegen die äußeren Widerstände, die wir messen können, sondern auch gegen innere Kräfte (Kohäsion, Affinität), die der Messung nicht zugänglich sind, Arbeit geleistet werden muss. Die folgenden Betrachtungen sollen zunächst zur Kenntnis dieses Gesetzes führen; dasselbe wird uns dann dazu dienen, rückwärts auf die Größe der Arbeit gegen innere Kräfte Schlüsse zu ziehen.*

3.   *Die Temperatur eines Körpers ist das Maß der in dem Körper vorhandenen Wärmemenge, d. h. der gesamten lebendigen Kraft der Wärmebewegung. Bei dem Nullpunkt der gewöhnlichen thermometrischen Skalen enthalten die Körper noch Wärme. Im Folgenden*

*soll immer nur von der so genannten absoluten Temperatur die Rede sein, die von einem Punkte an gezählt wird, bei welchem die Wärmebewegung wirklich aufhört. Dieser Nullpunkt der absoluten Temperatur liegt bei ca. -273° C nach einer Annahme, die später noch berührt werden soll. Die gesummte lebendige Kraft der Wärmebewegung ist dann der absoluten Temperatur geradezu proportional.*

4. *Denkt man sich die Wärmebewegung von den kleinsten Teilchen des Körpers ausgeführt, so ist die mittlere lebendige Kraft eines solchen Teilchens auch proportional der Temperatur; die Teilchen bewegen sich, mit einer durch die Temperatur bestimmten Geschwindigkeit, in gewissen Bahnen, die von dem sonstigen Zustand des Körpers abhängen. Die Bahnen z. B. der Sauerstoff- und Wasserstoffatome werden anders gestaltet sein, wenn sie in festem, flüssigen) oder gasförmigem Wasser, oder in einem Gasgemisch enthalten sind. Die Unterschiede, welche derselbe Stoff in diesen verschiedenen Zuständen zeigt, sind durch die verschiedene Gestalt der Bahnen bedingt; umgekehrt wird durch die Gestalt der Bahnen einer Anzahl Atome vollständig bestimmt sein, in welcher Weise dieselbe chemisch verbunden und welches der Aggregatzustand des Körpers, dem sie angehören, ist, mit welcher Geschwindigkeit sich auch die Atome bewegen mögen.*

5. *Es fragt sich nun noch, wie bei gleicher Temperatur in den verschiedenen Zuständen die mittleren Geschwindigkeiten verschiedener Atome sich zu einander verhalten; mit anderen Worten, ob die in dem Körper vorhandene Wärmemenge außer von der Temperatur auch von dem Zustand des Körpers abhängt. Dass Letzteres nicht der Fall sei, ist jedenfalls die einfachste und plausibelste Annahme in dieser Beziehung; schon deshalb, weil man einen Stoff in seinen verschiedenen Zuständen, z. B. Wasserstoff und Sauerstoff als Wasserdampf und als Gasgemisch, bei gleicher Temperatur in Berührung bringen kann, ohne dass sich die Temperatur ändert. Die mittlere lebendige Kraft der Atome ändert sich bei der Berührung nicht, weil sie schon vor der Berührung bei allen gleich groß gewesen ist. Diese Annahme stimmt überdies ziemlich gut mit gewissen Beobachtungen über die spezifische Wärme der*

*Gase, worauf hier nur hingewiesen werden soll [*)]. Wir setzen deshalb voraus, dass die mittlere lebendige Kraft der Atome und folglich auch ihre mittlere Geschwindigkeit nur von der Temperatur und nicht von der Gestalt der Bahnen, in welchen sie sich bewegen, abhängig ist.*

[*)] *Vgl. über diesen Gegenstand: Clausius, Abhandlungen I, 266 ff. und meine Bemerkungen – Ber. d. Deutsch. Chem. Ges., II, 725 ff."*

*"There are some chemical decomposition phenomena which were studied in more detail in the recent time that would for the first time allow for the consequent application of the Second Basic Law of thermodynamics. In such cases the heat decomposes chemical compounds and thus carries out a work against the forces called chemical affinities. Hence, it turns out, as has often been pointed out, that the doctrines summarizing the theory of heat in one sentence are also of great interest to chemists. Nevertheless, these teachings are known mostly to the physicists due to the fact that any rigorous derivation thereof could only be possible in using rather abstract mathematical considerations and along with this no truly popular representation is available. I would sincerely like to hope that my present exhibition of the theory of heat and its relevant results might perhaps contribute to their popularization. My present representation claims neither originality, nor severity; it is nothing more than an elementary way to try estimating the importance of the equations using known hypotheses.*

1. *Heat can be transformed into work and heat is generated from movement. Hence, we conclude that heat ought to be a movement itself; because even movement can be converted into work. The quantity of work which may arise this way is equal to the livening force – vis viva – of the movement, i.e. the half the product of the square of the velocity and the mass of the moving body. The same applies to the heat; a given quantity of heat represents a certain amount of kinetic energy equal to the work, which can be generated from the amount of heat. This is confirmed by the experience and builds up the contents of the First Basic Law of thermodynamics: work and heat are equivalent.*

2. *But the experience also teaches that not just any arbitrary amount of heat can be put into*

*operation without further consequences, and that in caloric machines the heat is always applied at a higher temperature. This indicates that it is just the temperature that determines how much work can be obtained from a given amount of heat. We may immediately confirm this, if we notice that the generation of work from heat always happens when, on the one hand, the body in question expands under the influence of heat and, on the other hand, it overcomes some resistance during this expansion. And the actual nature of the resistance to be overcome during the expansion is in fact very different from one kind of working body to another one. Still, such resistances are as a rule the greater the higher is the temperature in the same working body, as clearly demonstrated for gases and vapours, in particular. Therefore, the work, which can be carried out by the heat in such operations, increases with the temperature. But the particular law according to which such an increase in the amount of work takes place cannot immediately be derived from direct observation, because, in general, the work is to be done not only against some external effects which could in principle be measured, but also against some internal forces (like, e. g., cohesion, chemical affinity) where any measurement is either not accessible at all or truly difficult to access. This is why our following considerations should first lead to the formulation of the law in question. Then the latter will be used in trying to estimate the amount of the work against internal forces.*

3.   *The temperature of a body is a measure of the amount of the heat present in this body – that is, it is connected to the entire kinetic energy (livening force, vis viva) of the pertinent thermal motion. At the zero points of the ordinary thermometric scales the bodies under study ought to contain certain amount of heat as well. In the following, only the so-called absolute temperature will be used, which is counted from one specific point wherein all the thermal motion really stops. This zero point of the absolute temperature is about -273 °C, according to some assumptions which are to be considered later in more detail. Then the summary of all the kinetic energy of thermal motion ought to be approximately proportional to the actual absolute temperature.*

4.   *If one thinks of the thermal motion of the smallest particles in the working body under study, the average livening force/kinetic energy of such a particle is proportional to the temperature; all the particles move with a velocity determined by the temperature, in following certain paths/trajectories which depend on various conditions imposed by the actual working body, apart from temperature. For example, the trajectories of the oxygen and hydrogen atoms will be exhibiting quite different design, if the over-all movement takes place in the solid, liquid or gaseous water, or just in a gas mixture. The differences exhibited by the same substance in its various states are due to the different shape of the webs formed by the trajectories of the atomic movements. And, vice versa, the shape of the atomic orbits, the speed of the atomic movements, whether and/or how they are chemically bonded to each other will be fully determined by the physical state of the working body where the atoms belong to.*

5.   *Now the question is still remaining posed, as to the relationship among the mean velocities of different atoms to each other at the same temperature but in the different states of the working body under study; Or, in other words, whether the amount of heat present in the working body aside from the temperature is also dependent upon the state of the working body. That the latter should not be the case could at least be the simplest, straightforward and most plausible assumption – because you cannot bring a substance in its various states, for example, a water vapour and a mechanical gas mixture of hydrogen and oxygen, in contact to each other at the same temperature, but without changing the temperature. Indeed, the average kinetic energy of atoms shouldn't change after the contact, because it is already the same and quite large for all the participating atoms already before the contact. This assumption is also in pretty accordance with some actual observations on the specific heat of gases, what we would just like to mention here[*]. We assume, therefore, that the average kinetic energy of atoms and thus their average speed is dependent only on the temperature and not on the shape of the orbits which they follow during their movements.*

[*] *See on this subject: Clausius, Treatises I, 266 ff and my own remarks - Trans. German Chem. Soc., II, 725 ff."*

Of definite interest now would be to mention that Prof. Horstmann had managed to formulate the whole story even in a much more straightforward way than Prof. Gibbs at the same time, although, for the sake of historical and professional correctness, we conclude here that **_the both colleagues_** have opened the door to the correct formulation of thermodynamics, but couldn't go further themselves owing to the objective reasons… Indeed, Prof. Horstmann's story enables the modern reader to immediately envisage the computer methods of atomistic simulations, like the currently tried and true approaches – Molecular Dynamics (MD) and Monte Carlo (MC) … The only point which remains to be investigated would just be the pertinent interpretation of the MD and MC results …

Thus, both Prof. Gibbs and Prof. Horstmann were actively heading to the rational formulation of the Second basic Law of thermodynamics. And what were their results?

Prof. Horstmann [37]:

*"8. Jede solche Zustandsänderung, die sich durch äußeren Druck verhindern lässt, kann nun auch nach Willkür bei verschiedenen Temperaturen vor sich gehen lassen; man darf nur den Druck so groß machen, dass der Widerstand gegen die Zustandsänderung durch die Wärme bei der betreffenden Temperatur eben noch überwunden werden kann.*

*Die Arbeit, welche dabei geleistet wird, wächst wie der Widerstand; denn der andere Faktor, der Weg, welchen die Atome zurückzulegen haben, bleibt derselbe. Daraus folgt, nach dem was wir über den Widerstand wissen, dass die Gesamtarbeit, welche die Wärme bei irgendwelcher Zustandsänderung eines Körpers tun kann, proportional der absoluten Temperatur ist, bei welcher die Änderung geschieht. Dies ist das gesuchte Gesetz, welches nach Clausius, der es zuerst aufgestellt hat, benannt werden muss."*

*"8. Every state change of such a kind which might be thwarted by some external pressure, could still be triggered at different temperatures, if necessary; in such a case we may only render the pressure exactly so high that the very resistance to the change of state through the heat at the temperature under study can just be overcome.*

*The work done during such a process should grow together with the resistance; because the other factor, namely the way the atoms have to travel, remains*

*unchanged. It follows from what we know about the nature of resistance that the total work which produces the heat at any change of state of a body is proportional to the absolute temperature at which the change occurs. This is just the desired law which must be named after Clausius, who was the first one in suggesting it."*

The above citations from Prof. Horstmann pave a clear way to answering the questions, what is the physical sense of the 'entropy' notion, as well as, what Clausius was thinking of when introducing the latter. Prof. Horstmann was definitely not the only student of Clausius – but, most probably, one of a tiny number of truly attentive and thoughtful ones…

Prof. Gibbs (to the best of our knowledge, he had no idea as to the work by Prof. Horstmann):

In his work [34] Prof. Gibbs had carefully and in full detail analyzed the foundations of thermodynamics in the form they were known by the time of his publication, by considering the works by Sir W. Thomson, Prof. J. Thomson, R. Clausius, J. C. Maxwell, P. G. Tait (who pleaded for the "proper reconsideration" of the Clausius' 'entropy' notion), W. J. M. Rankine (one of the actual founders of the energetics we are discussing here) and, among other results, clearly underlined the relationship between the Clausius' 'entropy' notion and the Rankine's definition of 'thermodynamic function'.

And in his well-known following work [40], Prof. Gibbs had initiated a detailed discussion the physics and mathematics of equilibrium criteria and stability for different kinds of material systems, in starting from the Clausius' standpoint.

Interestingly, this discussion by Prof. Gibbs was analyzed by Prof. Dr. Wilhelm Ostwald who had come to the following conclusion [41]:

*"Mit der Auffassung der Energie als das allen anderen Grossen übergeordneten Hauptbegriffes geschah der Übergang von der unbewussten Energetik zur bewussten. Dass es sich hierbei wirklich um einen Schritt handelt, welcher noch zu tun war, geht beispielsweise aus der Tatsache hervor, dass W. Gibbs auf den ersten Seiten seiner großen Arbeit mit einigem Nachdruck eine (nach meiner Meinung nicht zutreffende) Symmetriebeziehung zwischen Energie und Entropie durchführt, also beide Grossen als entsprechende und daher in solchem Sinne gleichwertige behandelt. Mit jedem Schritt war nun die*

*Aufnahme der gesamten Ergebnisse der bisherigen Thermodynamik in die Energetik bewerkstelligt, und es ist durchaus nicht zulässig, beide in einen Gegensatz zu stellen."*

*"As soon as the energy notion could conceptually be placed over all other physical quantities, the energetics started to be fully conscious and thus ceased to be just intuitive. That such a move would still be an important step to go – can for example be demonstrated by the work of W. Gibbs, who is clearly insisting on a symmetric relationship (which is not appropriate, to my mind) between the energy and entropy, in that the latter both are corresponding, associated, correlated to each other, in that they are considered equivalent to each other. Such steps ought to contrive the incorporation of all the up-to-date thermodynamic results into the framework of energetics – and there remains no more contrast between the former and the latter".*

The Ostwald's work just cited above was in effect devoted to the debate with Prof. Max Planck and Prof. Ludwig Boltzmann, who were, instead, forcefully underlining the above-mentioned contrast between the energetics and thermodynamics – and promoting the statistical-physical standpoint.

It is important to mention here that Prof. Gibbs was aware of such debates – and his answer was to reconsider the foundations of the statistical mechanics on the basis of the rational thermodynamics [31]. But, to our sincere regret, he had not enough time to complete his studies…

Nonetheless, the Gibbs' results as for the canonic distributions are very well known, tried and true – and, meanwhile, not only in physical sciences, but in the theoretical economy as well [42-47]. The point of crucial interest for our present discussion is that the statistical-physical inferences of Prof. Gibbs are based upon a very strong approximation: the 'statistical independence'. In other words, the latter is a prerequisite of a complete absence or, at least, a considerable weakness of correlations between the elementary components of the system undergoing the statistical analysis, irrespective of the actual nature of such components (be they atoms/molecules/ enterprises … etc.).

Unlike in the field of physics (the rare, but fortunate exception is the work by Prof. Dr. B. H. Lavenda [48]), the economy theorists are actively and successfully looking at diverse fields not even in vicinity of their own – just to promote the proper development of the latter.

Thanks to such efforts due to colleagues in the field of theoretical economy, it is possible to get unbiased and instructive estimates for the validity boundaries of the Gibbs approximation.

Indeed, the equilibrium statistical thermodynamics by Gibbs works very well for a considerable number of economic problems in the form of maximum entropy analysis [42-46], and this success story could be summarized as follows [42]:

*"The relevance of statistical equilibrium as a model of real markets must eventually be judged in terms of its empirical explanatory power. The predictions of the theory will, of course, depend on the exact model, to which it is applied, that is, the specification of the offer sets of the agents. There are, however, a priori reasons, to think that the approach itself is quite general and robust.*

*The number of agents of each type must be large enough so that statistical considerations become of decisive importance. But the number of agents necessary to give maximum entropy methods explanatory force need not be astronomically large, even though the number of particles in most physical systems is astronomical. The statistical equilibrium concept should be relevant to the explanation of all but strictly oligopolistic and monopolistic markets.*

*At the most fundamental level, any maximum entropy analysis rests on an assumption that a certain set of possible transactions are all equally likely. The choice of a different set of transactions as equally likely could lead to a different prediction as to the distributional outcome. The offer sets in a statistical market model reflect all the relevant behavioral regularities of the agents, for example, any expectations agents have about their future transaction opportunities from past experience of similar markets. Thus, the easiest way to change the set of feasible market transactions is to propose a different model of offer sets.*

*The statistical approach to the analysis of phenomena involving a large number of essentially indistinguishable agents has been remarkably successful in physics – not least it suggests immediate and direct connections between empirically observed system-wide averages and the underlying micro-properties of the system. It should be possible to apply*

*the same methods to achieve a tighter connection between economic theory and observation."*

Thus, it is of crucial interest for our present discussion to learn how the 'oligopolistic' and 'monopolistic' markets are normally defined.

With this in mind, an oligopoly ought to be a market form in which a market is dominated by a small number of sellers (usually called 'oligopolists'). Along with this, it is clear that the enterprises forming such a market should always be in some competition among each other.

Further on, any kind of monopoly is connected with the competition as well. Remarkably, the latter is considered imperfect, in that, for example, there are many producers who sell products which differ from each other in some aspect(s), e. g., by branding or quality, and hence are in fact not perfect substitutes for one another. Moreover, every enterprise takes prices charged by its rivals as given and ignores the impact of its own prices on the prices of others.

Therefore, we may conclude that in the cases of monopolists and oligopolists the elements of the system under study couldn't anyway be considered fully uncorrelated or even weakly correlated, so that the canonic approximation by J. W. Gibbs can't be applicable in such cases already at the most fundamental level.

But now let us revert to the physical/chemical systems consisting of atoms/molecules. By theoretically assuming the statistical independence among the latter elements we are physically dealing with the so-called ideal gases/liquids/solids, where the systems' elements are capable of interacting with one another – if at all – then only by experiencing mutual perfectly rigid collisions.

The mathematics to describe such ideal situations is long and well known to be pretty simple – and, moreover, the ideal relationships between the pertinent observable variables describing the systems under study can explain a considerable number of experimental observations with enough grade of accuracy.

Still, in the actual physical/chemical systems the atoms/molecules are interacting with one another. In representing such interactions by means of the conventional mechanics, we need to define the interaction energy, which is correspondent to the potential energy of the system involved, that is, to the actual 'inventory of the available energy'. Then, it is just this inventory that might be used to find a 'driving energy' for performing some useful work (fully irrespective of our consideration level – macroscopic – mesoscopic – nanoscopic – microscopic).

To really use the potential energy, we first have to convert it somehow to the '*vis viva*', 'livening force', kinetic energy, which might be used – both – to perform the desired work (that is, to promote the system to reaching some desired result) – and – at the same time – to neutralize any possible hindrances on the way to the desired result …

Bearing all this in mind, we realize that if we would like to describe and study the mechanisms of some realistic processes (whatever level they might occur at !), we ought to skip the models of 'ideal substances' and take into account the realistic interactions among the relevant elements of the system involved.

It is also very important to note here that, in following the way described above, we are immediately facing a tremendous over-complication of our mathematical toolset, so that the only practicable way to study such systems would be computer-assisted molecular simulation methods, introduced already long ago and representing well-developed, clever, versatile toolsets [49-61]. Here we won't dwell on these approaches, but would like to stress that one of the most important points of any kind of molecular simulations ought to be the pertinent interpretation of their results.

## Energetics vs. Conventional Thermodynamics: True Physical Chemistry vs. 'Revolutionary Show Business'?

Of tremendous interest and crucial importance would be to monitor the development of the interrelationship between the energetics and the conventional thermodynamics.

To give the gist of a well-known Max Planck's saying – a scientific researcher should wait not for persuading his/her opponents, but for the passing of the latter…

Sure, this ought to be absolutely correct, if the scientific researcher in question would successfully like to combine his/her research with a kind of 'show business' (not only to solve some interesting and important scientific problem, but also to get as wide-

spread recognition of his/her achievements as possible)… Meanwhile, the scientific research, being richly colored by the diversity of interpersonal relationships, is stubbornly going its natural way, which is, first of all, ***Getting the Knowledge of the Truth***...

That the above statement isn't just an empty rhetoric could clearly be demonstrated by the development of the interrelationship between the energetics and the conventional thermodynamics.

We would like to start our consideration with the work by Lieut.-Col. Richard de Villamil and the reaction to it by Albert Einstein.

Lieut.-Col. Richard de Villamil (1850-1936) was an outstanding British military engineer, who, *inter alia,* was lively interested in physics and the legacy of Hon. Isaac Newton that is clearly reflected in his publications [3, 62-67]. His "Rational Mechanics" [3] is a detailed and logically consistent introduction into the field of energetics. Interestingly, in the 'Preface' chapter there he wrote as follows:

*"I have been asked:*

*Why I call this a book on 'Rational Mechanics'?*

*Do I not consider all Mechanics as being 'Rational'?*

*Using the word 'Rational' in its Dictionary sense of ,Agreeable to, or consistent with, reason,' I consider that much of it is hardly 'Rational'. …*

*… That this book may be considered as 'contentious' I quite expect. I might even confess that it is intentionally so; my object being to stimulate the Reader to think for himself, and not, necessarily, to bow down to 'Authority'. I do claim, however, and very strongly, that it is <u>not</u>, in any sense, '<u>Revolutionary</u>', since it is based on the solid foundation of the teaching of the greatest authors, from Newton downwards. Though there may not be very much that is either new or original in these chapters, nevertheless, there is a great deal that the student who studies only Text-books will find new, and, I trust, well worth study and attention.*

*My division of Mechanics into two branches – a <u>Deductive</u> and an <u>Inductive</u> branch – is, I fancy, new. In any case I do not know of anyone having definitely suggested it before, although its advantage – shall I say, its 'Rationality' – appears fairly obvious. Certainly M. Gandillot in his writings (Gauthier-Villars) implicitly suggests such a division; and Sig. G. Casazza*

*(Einstein e la Commedia Della Relatività) also suggests it. These authors distinguish between what they call Mechanics and Kinematics; Sig. Casazza saying (p. 20) that 'Einstein always confuses Mechanics and Kinematics' – i. e., 'Energetics and Pure Dynamics'.*

*I have brought forward the Principle of Least Action, or Least Resistance, very prominently. This principle, perhaps only second in importance to that of the Conservation of Energy, appears to be very little known, and is hardly referred to in Text-books, E. Mach's book on the <u>Science of Mechanics</u> being a brilliant exception.*

*I have only cursorily referred to the latest addition to Energetics, called the 'Quantum Theory', or 'Theory of Quanta'; that is the Theory that all Energy is transformed by 'jerks' or 'jumps' at <u>regular intervals,</u> and in <u>constant quantities</u>. I have, however pointed out this is a <u>logical deduction</u> from my explanation of viscosity, and <u>how</u> the molar kinetic energy is transformed into the 'shriller varieties' of Heat, Light and Electricity; these being generated in <u>Quanta</u>. The Theory of Quanta fits perfectly with Newtonian Mechanics; and is, indeed, a <u>logical necessity</u>. I even push the logical deduction further, and say that in Energetics there is no such thing as <u>uniform motion</u>; that all motion is accelerated by minute 'jerks'. In Pure Dynamics, of course, uniform motion is <u>assumed</u>; and there is an end of it. I have pointed out that Bertrand Russell holds that the Theory of Quanta cannot be reconciled and explained by Einsteinian Mechanics.*

*I have thus milked many cows, but the <u>cheese is my own</u>. My object has been, not to introduce innovations, but to try to introduce some system into the heap of facts discovered by others – but which have been neglected. My chief aim is to interest the student, and not to bore him."*

Prof. Dr. Albert Einstein could have delivered his rejoinder in writing a Foreword to the book by Lieut.-Col. de Villamil devoted to the legacy of Hon. Isaac Newton. That book was written and published, according to the Author's claim, just to show the role of Newton's personality in his seminal work – first of all, the Newton's contributions to the Physics [67].

Lieut.-Col. de Villamil had written as follows:

*… "It is unfortunately the fashion, at the present day, to view Newton as a 'Mathematician', the only part of his <u>Principia</u> which is now commonly read being Book I which is purely mathematical. Newton was not*

*however a mathematician first and before all. He was essentially a 'Physicist'; who undoubtedly used mathematics as his chief 'tool'. He was referred to by his contemporaries as a 'Mathematico-Physicist' – his correct title; whereas most of his modern successors would be best described as 'Physico-Mathematicians'."* …

Whereas Prof. Einstein had written the following very polite, but, in effect, clearly slighting words:

*"Colonel de Villamil deserves the thanks and congratulations of physicists throughout the world for the industry and ingenuity that enabled him to recover for us the substantial remains of Newton's Library, the complete catalogue of the books that he owned and the inventory of all his belongings.*

*These make it possible for us to frame a realistic picture of a man as he lived and worked, the picture that has a real atmosphere very much more substantial than the old legend of the apple in the orchard.*

*… The record will be indispensable for those who wish to see Newton in his proper perspective.*

*From the standpoint of mathematical history, all mathematicians will be keenly interested in Colonel de Villamil's suggestion that Newton was the inventor of the calculus of variations, justly attributed by priority of publication to Lagrange. The suggestion would provide a solution for the problem as to how certain of the results which he obtained could have been determined, and deserves careful critical examination. …"*

Well, what were those 'attacks' at A. Einstein's achievements – just wild outpours from people consumed and green with envy? Or still something more than such trivial guises? And was/is the work and legacy of Hon. Isaac Newton over- or underestimated?

The answer to those questions could easily be found in the literature. We would like to start with considering the problems with the Newtonian work and legacy. All the problems in this connection have been carefully analyzed most recently [68]. We send the interested readers to the latter literature reference by concluding that, as Colonel de Villamil had duly noticed, Hon. Isaac Newton was not a kind of Divinity, but just a normal human being with his own pros and contras, pluses and minuses – he wasn't ever a 'know-it-all' and he could definitely 'slip a cog' – as everybody of us upon Earth…

Meanwhile, the legacy of Prof. Dr. A. Einstein himself would definitely deserve a closer look, for it seems to be related to our present discussion.

First of all, let us have a look at the analysis carried out by Prof. Dr. Daniel Berthelot (1865-1927), an outstanding French physicist-chemist, son of the well-known French chemist Prof. Dr. Marcelin Berthelot. Prof. D. Berthelot was keenly interested in Einstein's work and had published his detailed thoughts on the theme [69, 71].

The authentic manuscript of Prof. D. Berthelot's last publication was on auction sale at Christie's in Paris on 29 November 2005 as a Lot 187/Sale 5415 [72]. This manuscript is dated by the year 1920 and resulted from the lecture Prof. D. Berthelot delivered in February, 1909 for the French Society of Electric Engineers. To increase the value of the object to sell, Christie's noticed that the candidacy of Prof. D. Berthelot was suggested for the Nobel Price in the year 1907… And the question could immediately be posed – who was Daniel Berthelot in effect? For, we seem to know practically nothing about him…

Fortunately, there have been several most recent illuminating publications about his life and work [73-75] that are revealing a colleague who had devoted his whole life to scientific research and delivered serious contributions to the whole field of physical chemistry.

The only question remains after reading the investigation [73-75]: Why at all he was dealing with the relativity theory of Einstein? One possible answer could be, for he was seriously dealing with the foundations of thermodynamics [73]... Remarkably, his standpoint as concerns the work by A. Einstein was throughout critical. Above, as we discussed the Richard de Villamil's contributions to energetics, we have already encountered some criticism of Einstein's relativity theory. On the other hand, a number of apologetic books about Albert Einstein have been published in different languages (including their authorized translations), where the criticism involved is more or less skillfully slighted [76-78]…

And now, it is of interest to have a closer look at Prof, D. Berthelot's standpoint. In particular, he wrote [70]:

*"Le trait le plus saillant de la doctrine de la relativité est la négation de l'idée du temps, telle qu'on l'a conçue, depuis qu'il y a des hommes et qui pensent,*

*pour parler comme Jean de* **La Bruyère** *(1645 – 1696)."*

*"The most salient feature of the relativity doctrine is the negation of the idea of time, for the former was designed using the fact that 'there are people, and they are capable of thinking', to put it in the way similar to Jean de La Bruyère (1645 - 1696)."*

Of interest for this philosophic, methodological theme would also be the book by Martin Johnson [79], as well as the work by Prof. Dr. E. A. Milne [80]. Moreover, the work and ideas of the prominent Japanese mathematician Prof. Dr. Kiyoshi Oka (1901-1978) should be mentioned here [81, 82].

Indeed, in our most recent work [18] we have presented a discussion about the sense 'Ji' (= 'Toki' in Japanese) as given by an ancient Chinese philosophy book, 'I-Ching' (that should be read as 'Eki-kyo' – or more shortly 'Eki' – in Japanese).

Prof. Kiyoshi Oka is well known as a founder of the multi-complex variable function theory, presenting the concept of sheaves etc.

Aside from this, he mentioned how important ought to be the difference between the time as a coordinate in math and the time we feel as 'Toki' = 'time being', or 'the life time'.

Prof. Oka had consequently put his standpoint in detail as follows:

'The science is perfectly wrong. This is because in science, from the beginning on, the physicists put a gloss on the coordinate systems including time axis, but this cannot reflect the true Nature. There is no time, no space, but the Universe is constructed by 'Jo（情）' or 'Jocho（情緒）' which is sometimes translated into English as 'emotion' – but, in effect, it is very difficult to adequately translate this into the Western languages in a short phrase.

In more detail, the notion of 'Jocho' could be summarized as follows:

(A)    A capability of learning based upon intellectual and sensory factors.

(B)    A capability of building and/or maintaining satisfactory interpersonal relationships with surrounding persons.

(C)    Appropriate types of behavior or feelings under normal circumstances.

(D)    A capability of overcoming physical symptoms or fears associated with normal everyday problems.

Further, Prof. Oka said: "'Toki' that we feel is different from "time" such as a parameter for dynamics, since 'Toki' is only passing after the events. Namely, time in the future and time in the past are not the same – they do have different sense as compared to each other. Nonetheless, physicists never think in this way. Hence, the science is wrong!"

Interestingly, the ideas of Prof. Oka are in full accord with the notion of time defined by the prominent French philosopher Henri Bergson (This is not surprising, because Prof. Oka had spent a considerable time to study mathematics in France). Henri Bergson was never involved into any research in the field of Natural Sciences – he was all his life long – and still remains in our memories as – An Outstanding Poet… Nonetheless, he was extremely interested in the results brought by the natural sciences and was in active correspondence with the physicists who were philosophers as well, like Prof. Dr. Ernst Mach, e. g….

Henri Bergson's concept of time could be summarized as follows [83-85]:

Any feeling in itself ought to represent a pure quality, but if viewed through the prism of space, the feeling turns into an amount or intensity. Consequently, the formation of the "*facts of perception*" based upon the "*facts of reality*" indicates a change in the forms of reality: Thus, the reality acquires the form of perception.

Bergson connects such a false impression as to the nature of perception with the eradication of real time out of the science. The science in general and the psychological science in particular operate solely with an abstraction of time. Bergson explains the notion of time abstraction using the following example: "*Despite all the movements in the universe would somehow two or three times faster, all our mathematical formulas together with all their constituent elements would not change, because the number of simultaneities in space would remain the same*". Therefore, Bergson concludes, the science, and especially its branch of mechanics, considers the time to be nothing more than a sheer simultaneity, and consequently the motion – nothing more than a sheer stillness.

In contrast to the spatial (non-temporal, non-intrinsic) understanding of time Bergson suggests viewing the time as a "*means of duration*", as a "*process of continuous formation*", and definitely not just as a "*fait accompli*", not as a result expressed by some peculiar algebraic equation. Sure, the available algebra might still express "the duration time" and/or "the position in space occupied by the moving body" in its formulas, but it is sheer incapable of revealing the duration and the movement as they in effect are. The zest here consists in that "*the duration, the motion might be conceivable as the products of the pertinent presumable syntheses and not as particular things themselves*". Although moving bodies have to sequentially pass through all the points on some rectilinear (curvilinear) trajectory, the movement as it is has in effect nothing to do with the latter.

And to finalize the critical discussion about Albert Einstein's doctrine, we have to cite the conclusion drawn by Prof. Dr. Max Bernhard Weinstein (1852-1918) in his detailed book devoted to the foundations of the relativity theory [86]. It is important to note here that Prof. Dr. M. B. Weinstein was an outstanding German physicist and philosopher, at his time he was successfully holding lectures in these fields at the Humboldt University of Berlin. Nonetheless, apologetic books slight him down to a 'one popularizer' (cf., e. g., [77])… This remarkable standpoint is as follows:

*"As word of Einstein's accomplishment spread in Germany, more sensational articles appeared in newspapers. They kindled darker reactions to Einstein's theory, fuelled by political unrest and the duress of war. One popularizer, Max Weinstein, claimed that, general relativity had removed gravity from its earlier isolated position and made it into a 'world power' controlling the laws of nature. He warned that physics and mathematics would have to be revised. …"*

Still, what Prof. Weinstein had communicated sounds in effect but quite different way [86]:

*"(Page 287) … Wird die Lichtgeschwindigkeit übertroffen, so geht die Fläche für den ruhenden Beobachter ins unvorstellbare über, indes sie dann für den bewegten Beobachter real vorhanden ist. Um dieser Folgerung auszuweichen, hat man angenommen, dass Bewegungen mit Überlichtgeschwindigkeit unmöglich seien. Das ist gar nicht nötig, wenn man sich auf das beschränkt, auf was die Theorie allein sich bezieht, auf*

*Strahlenverhältnisse; werden Strahlen noch rascher fortgeführt, als sie sich verbreiten, so verbreiten sie sich für einen ruhenden Beobachter eben nicht, sie können keinen Punkt des Raumes des Beobachters erreichen, weil er ihnen schon vorher entrückt ist.*

*Ähnlich sieht es mit einer entsprechenden Folgerung hinsichtlich der Zeit. Die Lage einer Uhr des Relativsystems im ruhenden System sei gegeben durch die Koordinaten x, 0, 0. Dann ist x = p t (hier: die Geschwindigkeit mal Zeit). Also wird die Relativzeit*

$$\tau = \frac{1}{\sqrt{1-\frac{p^2}{V^2}}}\left(t - \frac{p}{V^2}x\right) = t\sqrt{1-\frac{p^2}{V^2}}.$$

*Ist p = V (V ist hier die Lichtgeschwindigkeit), so wird τ = 0, für den ruhenden Beobachter schreitet die Zeit im Relativsystemüberhaupt nicht fort, sie deutet ihm dort immer Gegenwart. Ein mittelalterlicher Philosoph hat die Behauptung aufgestellt, dass für Gott die Zeit überhaupt absolute Gegenwart bleibt. Dieser Gedanke ist sehr hoch und bedeutend. Aber dem Relativiker selbstverständlich, wenn die Welt mit Lichtgeschwindigkeit durch den Raum jagen sollte. Allgemein bleibt dem ruhenden Beobachter die Relativzeit gegen seine Zeit stets zurück um den Betrag*

$$\Delta t = \left(1 - \sqrt{1-\frac{p^2}{V^2}}\right)t.$$

*Hieraus schließt Einstein, dass wenn man von zwei an einem Ort synchron gehenden Uhren eine auf einer beliebigen Kurve bewegt und zur anderen zurückführt, dass sie dann dieser gegenüber zurückgeblieben sich zeigen muss. Allein die Uhr als Mechanismus ist nicht zurückgeblieben, nur die Kontrollen nach der Definition mittels Strahlen zeigen auf dem Wege ein Zurückbleiben an. Am Ausgangspunkt zurückgekehrt, findet man durch gleiche Kontrolle wieder Synchronismus. Das ganze Betrifft wieder nur Strahlenverhältnisse, nicht das Verhalten von Gegenständen."*

*"(Page 287) … If the velocity of light could be outdone, then the whole area goes over to the unimaginable for the stationary observer, but remains quite perceptible for the motile observer. To avoid drawing such a conclusion it is suggested that motions with any velocity greater than that of light are sheer impossible. But in effect such a suggestion is not*

*necessary, for it is enough to be dealing with the same object that the theory is describing, namely with the conditions of the irradiation; indeed, if the irradiation is performed in a faster way than the velocity of light, then the radiation isn't propagating for a stationary observer, for it isn't reaching any point of the observer's location, for the observer had already escaped from it.*

*A quite similar story could actually be told about the time as well. Let the position of some clock in the relative system be described in the stationary system through the coordinates set x, 0, 0. Then x = p t should be true (*here: coordinate is the velocity times time*). Hence the relative time can be cast as follows*

$$\tau = \frac{1}{\sqrt{1 - \frac{p^2}{V^2}}} \left( t - \frac{p}{V^2} x \right) = t \sqrt{1 - \frac{p^2}{V^2}}.$$

*Now, if p = V here (*V stands here for the velocity of light*), then τ = 0, that is, for the stationary observer the time in the relative system is completely stopped, the time remains in the current moment for ever. A mediaeval philosopher stated once that the time for the Lord Almighty remains for ever the absolute current moment. This is very solemn and significant idea! But for the adepts of the relativity theory it is taken for granted that the Whole World is doing nothing more than just moving through the Space with the velocity of light. In general the relative time for the stationary observer is still belated with the following time difference*

$$\Delta t = \left( 1 - \sqrt{1 - \frac{p^2}{V^2}} \right) t.$$

*Here Einstein concludes as follows: If of the two synchronously going clocks placed at one and the same position the one will be brought along some curvilinear trajectory farther from and then closer to the other one, then the former one should look like stopped from the standpoint of the latter one. But the clock itself isn't stopped, only the control of its state using radiation will exhibit stopping on the clock's way. After returning the clock to its initial position we shall detect in the same way the two synchronous clocks again. All the story is then about the experimental conditions connected with radiation, but not about the processes in the real objects."*

The main point of the above-cited part is that – the Einstein's theory concerns the irradiation relations of the pertinent experiments **only**, but not the actual

physics of the processes under study. Still, Prof. Weinstein demonstrates here clearly how an apologetically blind following Einstein's theory might in fact 'destroy' the actual space and time in our perceivable world (what Henri Bergson and Kiyoshi Oka were in fact protesting against!).

And, apart from Prof. Weinstein's and Prof. Berthelot's criticisms discussed above, it is important to note here that, in effect, it looks like this notorious 'getting rid of time' ought to be the important logical basis for over-interpreting the ingenious cyclic model of Nicolas Leonard Sadi Carnot – and, as a result, the 'burial' of the conventional thermodynamics...

Remarkably, in this connection, Prof. Weinstein had also put under detailed scrutiny the striving of Albert Einstein and Max Planck to reformulate the conventional thermodynamics in terms of relativity theory. Here the following citation is of crucial significance for our present discussion.

*„(Pages 341, 342) … Ich stelle nochmals die Annahmen zusammen, unter denen die vorstehenden Entwickelungen gelten*

1.   *Das Punktsystem befindet sich in stationärem Zustand.*

2.   *Das thermokinetische H Potential hängt dann nicht von den Lagen der einzelnen Teile des Systems ab, auch nicht von der Richtung der einzelnen Bewegungen, sondern nur von der lebendigen Kraft der Gesamtbewegung, von der Dichte und von der Temperatur.*

3.   *Bei der* Lorentz-Einstein*-Transformation ändern sich die transversalen Kräfte …, die für elektrodynamische Verhältnisse der* Einstein*'schen Umrechnung gemäß den* Maxwell*'schen Ruhegleichungen entsprechen. Und für stationäre Systeme allgemein gelten sollen.*

4.   *Ein Weltraumelement im Sinne* Minkowskis *soll für alle Transformationen nach* Lorentz-Einstein *invariant sein.*

5.   *Vorgänge, die nach Zeit und Ort in einem Bezugssystem umkehrbar sind, sollen umkehrbar bleiben, wenn sie nach Zeit und Ort eines anderen, im Sinne der* Lorentz-Einstein*'schen Transformation abgeleiteten Bezugssystems verlaufen.*

*Keine dieser Annahmen – mit Ausnahme der vierten, wenn man das Relativitätsprinzip im Sinne <u>Minkowskis</u> auffasst – liegt im Relativitätsprinzip selbst. Was <u>Einsteins</u> Formeln nur lehren können ist hervorgehoben. Bei der fünften Annahme könnte man glauben, dass sie unmittelbar aus dem Relativitätsprinzip fließe. Allein dieses bezieht sich auf die mathematische Form der Gesetze der Vorgänge, nicht auf die Vorgänge selbst. Das Gesetz der Umkehrbarkeit bleibt bei der Transformation erhalten, es ist wieder*

$$dS' = \frac{dQ'}{\vartheta'}.$$

*Aber ob die Umkehrbarkeit selbst erhalten bleibt, ist eine ganz andere Frage. Indessen wird das Relativitätsprinzip überhaupt weit über seinen Ausspruch hinaus angewendet. Der Anwendung entsprechend müsste ihm folgende Fassung gegeben werden.*

<u>*Eine und dieselbe Erscheinung verläuft physikalisch für zwei gegeneinander gleichförmig und parallel bewegte Beobachter in gleicher Weise, und die Gesetze dieses Verlaufes sind für beide Beobachter ebenfalls die gleichen, falls die Raum-Zeit-Systeme der beiden Beobachter zueinander nach den Lorentz-Einstein'schen oder, allgemeiner, Minkowski'schen Formeln geregelt werden. Erscheinungen gleicher Art behalten für einen Beobachter physikalisch ihr Verhältnis zueinander, auch wenn sie ihre gegeneinander in gleichförmiger Bewegung befindlichen Raum-Zeit-Systeme vertauschen, falls diese Systeme für den Beobachter in den von Lorentz und Einstein, allgemein von Minkowki, aufgestellten Beziehungen stehen.*</u>

*Ob das Relativitätsprinzip in diesem auch das rein Physikalische einbeziehenden Umfange gerechtfertigt wird, ist noch weit zweifelhafter, als ob es in der Beschränkung allein auf die mathematischen Gesetze einer Erscheinung als gültig angesehen werden darf, in der es nichts weiter aussagt, als dass diese Gesetze für alle zueinander in gleichförmiger Parallelbewegung befindlichen Systeme den gleichen Ausdruck durch die zugehörigen Koordinaten und die zugehörige Zeit haben, und dass man dabei die Gesetze von einem System zum anderen und von einer Zeit zur anderen mittels der Lorentz-Einstein'schen, allgemeiner mittels der Minkowski'schen Gleichungen überträgt. …"*

<u>(Pages 341, 342)</u> *… I would greatly appreciate summarizing once more all the assumptions necessary for the theory described above to be valid.*

1.    *The point system is in its stationary state.*

2.    *The thermokinetic potential H is then independent of the position of each separate part of the system, as well as of the directionality of every separate motion modus – it is dependent only on the livening force of the movement as a whole, on the density and the temperature.*

3.    *With the help of the <u>Lorentz-Einstein</u> transformation those transversal forces are changed which are correspondent to the electro-dynamic conditions of the <u>Einstein</u>'s transformation according to the <u>Maxwell</u>'s equations in the stationary system. Hence, they ought to be valid for stationary systems in general.*

4.    *An element of the space in the sense of <u>Minkowski</u> should be invariant for all the transformations according to <u>Lorentz-Einstein</u>.*

5.    *The processes being reversible in the space and time in one coordinate system should remain reversible when they proceed in the time and space in some other coordinate system inferred from the former one with the help of the <u>Lorentz-Einstein</u>'s transformation.*

*None of the above assumptions is contained in the principle of relativity itself – aside from the 4th one, if we grasp the relativity principle in the sense of Minkowski. And we have already seen the most of what could be communicated by <u>Einstein's</u> formulas. Thus, one might believe that solely the fifth assumption could be deduced directly from the relativity principle. Meanwhile, even this assumption is connected with the mathematical form of the laws for the course of events, but not with the events themselves. The law of reversibility is conserved during the transformation, and we get the same original result of Clausius*

$$dS' = \frac{dQ'}{\vartheta'}.$$

*But whether the reversibility **itself** could be preserved is a quite different problem. This is why such an application of the relativity principle goes anyway far beyond its actual dictum. Hence, the following*

*formulation ought to be suggested in correspondence with the application of this principle.*

*One and the same process goes physically in the same direction for two observers uniformly moving with respect and in parallel to each other, and the laws of the relevant process are then for the both observers also the same, if the space-time systems of the two observers are regulated by the Lorentz-Einstein or, more generally, by Minkowski formulas. Phenomena of the same kind will keep for an observer their physical relationship to each other, even if they swap their space-time systems uniformly moving with respect to each other, whereas these systems are related for the observer by the Lorentz-Einstein, or, more generally, by the Minkowski transformations.*

*It is throughout much more questionable, whether the relativity principle could be justifiable also in some purely physical sense. For the point is that such a principle cannot be much more meaningful than we could have seen in the above paragraph. … "*

All the above-cited thoughts of Prof. Weinstein clearly show his perfect professionalism and complete fairness. Still, to fetch his books is a non-trivial task in Germany. Most probably, lots of them were demolished during the Hitler's time – for Prof. Weinstein was of Jewish origin… Albert Einstein had also difficult time in connection with the same political situation in Germany… Remarkably, while rightfully criticizing Einstein's relativity theory, Prof. D. Berthelot [70] tends to ascribe the undesirable features of Einstein's theory back to the 'eternal revolutionary spirit of the Jewish nation' by comparing Einstein's activity to that by Karl Marx, Trotsky and Zinovieff…

Surely, taking into account what happened to Einstein in particular – and so many other people, in general – it is definitely unfair to punctuate the national features of the problem in question!

Meanwhile, as regards Einstein's relativity theory itself, this 'revolutionary sounding' 'negation of the space and time' stubbornly accompanying the latter, had and has most probably nothing to do with any political/national situation, but, as Prof. Berthelot had justly stressed – simply with some strange processes in the brains of thinking people… or, may perhaps, with the purely natural strive for recognition – if so, then – as wide as possible – which is to some extent cultivated in each of us… But those who intentionally place such strive into the center of their living activities are normally denoted as 'show-businessmen'…

Anyway, to our regret, it is this '*negation of time and space*' that could most probably play its role in the 'revolutionary thwarting' of the conventional thermodynamics – and Prof. Weinstein, after publishing his detailed account of the theory, tried to warn the colleagues by submitting a paper into a 'popular' scientific journal – with the following very important statement [87]:

*"…als die Bedeutung dieses Prinzips … so ins ungemessene ausgedehnt worden ist, dass zu den törichtsten Behauptungen eine unerträgliche Unduldsamkeit gegen anders Meinende sich gesellt hat, die fast einem mittelalterlichen Glaubenszwang gleicht."*

*"As soon as the significance of this principle … was widened to the extent that there is presently an unbearable intolerance in response to dissenting persons which is nearly similar to a kind of the mediaeval compulsory faith."*

And this sincere, justified and, as we could see, fully vindicated warning has somehow gone unheeded [77], especially as we shall see in detail from our further discussion.

## Synergetics: Pros and Contras

The revolutionary spirit in the physics of the twentieth century beginning was connected first of all with the transition to the microscopic (atomic/ molecular) level of scientific research. Together with this, there was a definite trend to skip all the classical physics by trying to look for some 'specifically microscopic' physical laws which, in connection with the statistics, could 'explain' the conventional macroscopic laws…

Most recently, we have analyzed the current state of art in the fields of thermodynamics and statistical mechanics [18] and pointed out some conceptual problems, as well as some possible ways of trying to solve the latter. In the present report we would greatly appreciate to continue the analysis. This is why; we would now like to have a look at the so-called non-equilibrium thermodynamics, especially at its development after the breakthrough by Lars Onsager.

The true work on the subject was restarted after the Second World War, so that we might mention a number of works [88-96]. And of special interest are the works of those colleagues who were dealing with the thermodynamics of living systems, for here the problem of non-equilibrium was and still is of crucial importance [97-99].

But there is a work area in the field deserving our special attention – this is the activity of Prof. Dr. I. R. Prigogine, his allies and co-authors. This work area bears presently the name of 'Synergetics', so we start first of all with the apologetic description of the latter. The Synergetics can be considered a rather new interdisciplinary field and direction of scientific research. During the relatively short time of its development, the Synergetics was repeatedly triggering truly cross-disciplinary and even cross-cultural research activities. Not only physicists, biologists and mathematicians, but even historians, sociologists, psychologists, linguists, ecologists, economists, theologists and culture scientists are as well immensely attracted by both the novelty and rediscovery of scientific and cultural traditions in this lively pulsating field. It is also important to add here that the emergence of Synergetics had triggered an intensive development of such a useful field as the 'non-linear dynamics' [100].

The initiator of the work in the above-mentioned direction(s) was definitely Prof. Dr. I. R. Prigogine (1917-2003). The readership might get full information about him by going to the following references [101, 102]. And here we would just like to analyze the contribution of Prof. Prigogine in full detail – with respect to our main theme.

Remarkably, already in his student's time Prof. Prigogine was lively interested in the philosophy of physics [103, 104]. Already in his student's essays he demonstrates his lively sympathy with the revolutionary ideas in the natural sciences of the XX century. And then, later on, he was eager to embody all the new research trends of the beginning of the XX-th century. Let us now follow his earlier works [105-113]. Of especial importance is one of the earlier theses of Prof. Prigogine, where he puts his main idea in detail, namely the idea of the 'thermodynamic time'.

What is the physical sense of the 'thermodynamic time' notion? Here we cite Prof. Prigogine as follows [108]:

<u>"Caractéristiques du temps thermodynamique</u>

*Nous pouvons résumer comme suit les principales caractéristiques du temps thermodynamique:*

*Le temps thermodynamique est non-metrique, c'est-a-dire qu'il ne se reduit pas a la mesure des longueurs. Il est au contraire arithmetique car la source d'entropie introduissant des vitesses reactionnelles chimiques, sa determination exige le denombrement de particules.*

*Issu du seconde principe, le temps thermodynamique apparait necessairement comme une notion statistique. Il perd son sens simple a l'echelle des processus elementaires.*

*Enfin, le temps thermodynamique est essentiellement local. Il est engendre par les processus irreversibles qui se passent a une endroit bien determine de l'espace.*

*Notons, que dans notre theorie elementaire, non-relativiste, le temps astronomique et le temps thermodynamique sont lies par la formule de transformation simple (13.4). Il n'en sera plus de meme dans une theorie plus generale invariantive ou apparaitra une difference fondamentale entre le temps thermodynamique defini a partir d'un invariant, l'entropie, et le temps ordinaire defini comme quatrieme composant d'un vecteur (1).*

*(Cf. E. A. Milne [80, 114, 115], qui distingue tres clairement le temps 'newtonien' du 'temps du probabilite' ou 'temps du radioactivite'. Cette derniere conception est tres proche du temps thermodynamique."*

<u>*"The characteristics of the thermodynamic time*</u>

*We can now summarize the main features of the thermodynamic time:*

*The thermodynamic time is not metric, that is, it can not be reduced to a length measurement. Instead, it is algebraic, because the determination of the entropy source during the introduction of chemical reaction rates requires enumeration of the particles.*

*According to the second principle, the thermodynamic time is necessarily introduced as a statistical concept. But it loses its simple meaning at the scale of elementary processes.*

*Finally, the thermodynamic time ought to be essentially local. It occurs due to irreversible processes and has a well-defined point in the space.*

*Note that in our elementary non-relativistic theory the conventional astronomical time can always be transformed into the thermodynamic time by the simple formula (13.4). Even in a more general theory there ought to be substantial difference between the thermodynamic time, which is defined by an invariant, the entropy, and the ordinary time which should be displayed as a fourth component of a vector (1).*

(1) *See E. A. Milne [80, 114, 115], who very clearly distinguishes among the "Newtonian" time, "probability time" or "radioactivity time". The latter concept is very close to the thermodynamic time."*

Here we encounter an example of a really wild interpretation of the 'old good' Boltzmann-Planck expression for entropy *via* the "probability of the macro-state". This becomes clear from Prof. Prigogine's phrase about the 'thermodynamic time' as a 'statistical concept'.

Of extreme interest and importance for our present discussion are the following features of the 'thermodynamic time':

a)   It is ___non-metric___ – that means nothing more that it cannot in principle be measured in the conventional direct way, although it is nonetheless ___algebraic___… Hence, the question should immediately be posed – what is in effect the connection of this notion to the actual physics?

b)   It is a ___statistical concept___… And it is exactly here that the poser about the physical sense of the notion involved becomes rhetoric…

The only valid conclusion to be drawn – here we deal with the case where the difference between the '*Mathematico-Physicists*' and '*Physico-Mathematicians*', as suggested by Lieut.-Col. Richard de Villamil, becomes truly obvious. Moreover, here we see the bright example of how to effectively '*get rid of the actual ordinary time*' by a number of skillful mathematical prestidigitations, in accordance with the forceful warnings by late Prof. M. B. Weinstein and late Prof. D. Berthelot...

Moreover, all these prestidigitations with time are in marked contrast with respect to the suggestions by Henri Bergson and Kiyoshi Oka… The only colleague, whose work we have rediscovered most recently, and who had managed to fruitfully consider and employ the notion of time which is at least not running fully afoul of Bergson's and Oka's suggestions, was Dr. Georg(e) Augustus Linhart (see the work [116] and the references therein). A propos, Dr. Linhart could also suggest the physically fully clear relationship between the time and entropy: he considered time as a *thermodynamically intensive variable* – and nothing more than that… Such a suggestion allows a – possibly not quite expected, but still pertinent – incorporation of

the energetics' standpoint into the conventional thermodynamics... However, with this in mind, we would greatly appreciate to transfer this interesting and important discussion to elsewhere, although we have already started to discuss this topic somewhat earlier [18].

Finally, it is also important to mention here that the ideas of Prof. I. R. Prigogine [117] and his school were more or less heavily criticized from very different standpoints [118-122]. To our mind, such criticisms are fully justified for the researchers' community – this is definitely not devaluating the achievements of all the synergetics' adepts – and will never close the ways for the further development of this very interesting and important branch of physical mathematics (among the newest treatises in the field, cf. [123]).

The only really regrettable minus of this whole story is that the school of Prof. Dr. Théophile de Donder, as well as other colleagues, were actually heading to a very interesting and important result – to establishing valid formal links between the energetics and the J. W. Gibbs train of thoughts (cf. their publications [124-136]). But their successful work, the efficiency of the propagation of their ideas were thwarted, to our sincere regret – mostly owing to the natural reasons, like the World War and the ineluctable departures of the colleagues mentioned, as well as due to the activities of Prof. I. R. Prigogine and his school… To be mentioned separately in this connection are also the works of such outstanding colleagues as Prof. Dr. J. Timmermans [137, 138], Prof. Dr. G. van Lerberghe [139, 140] – and (the last but not the least!) the book by Prof. Dr. P. Walden [141] who presented and analyzed the history of the studies performed by the predecessors of the latter outstanding colleagues. Now, it seems to be just the perfect time to revert to the legacy of de Donder's, Timmermans' and van Lerberghe's schools, their trains of thoughts – and pertinently refresh it…

## Energetics and its Development in the XX-th Century

Meanwhile, one cannot draw a conclusion that there was and is absolutely no interrelationship between the energetics and thermodynamics. Both chemists and physicists were and are actively working on (re)establishing and strengthening such an interconnection.

Still, along with the latter positive work direction there was and is a clear negative trend, to recklessly

insert the (to our sincere regret!) unfinished works of Prof. Gibbs and Prof. Boltzmann into the general framework of physical chemistry by producing absurdities like "*entropy is a measure of disorder*", "*entropy is evil*", "*thermodynamic time*", etc…

Especially difficult situation remains in the field of the chemical thermodynamics. Although there were lots of attempts to bridge the gap between chemistry and thermodynamics in a number of ways (there is a wealth of works, but just to name a few we haven't mentioned in our earlier review [18] – please, cf. [142-145]). Remarkably, the book [145] is dealing in detail with the Third Basic Law of Thermodynamics – the well known Nernst Law [146], which is in fact truly argumentative, as we have already seen [18] … But only rare workers refer to the books by a Dutch thermodynamicist Prof. Dr. J. J. van Laar [147, 148], who was quite a definite adept of the 'energetics' – and he was referring to both Wilhelm Ostwald and Josiah Willard Gibbs…

But, interestingly, practically ___**nobody**___ all over the world was and is referring to Prof. Dr. Horstmann (cf. a careful analysis of Horstmann's life and work published in [149]). In Germany itself, the only colleague, who could explicitly estimate Horstmann's contribution, was Wilhelm Ostwald. Also in the USSR – the only outstanding thermodynamicist who had really honored Prof. Horstmann's achievements was Isaak Ruvimovič Kričevskij [150-152].

And in France, as we have already seen, Prof. Dr. Pierre Duhem knew about the work of Prof. Horstmann and he was furthermore an enthusiastic adept of energetics [32, 153]. Most probably, it is Duhem's authority that initiated lively interest in the field of energetics among French physicists and chemists. As a result, there were a number of very active and proactive French workers in this field [154-168]. Both Prof. Michaud and Prof. Dodé really deserve full respect, for they were truly ___**Scientific Research Workers**___ – they were successfully continuing their research work even during the Hitler's occupation of their country.

In the XX-th century Europe there was also one more notable adept of the energetics, namely, Prof. Dr. Johannes Nicolaus Brønsted (1879-1947). Among other serious contributions to the whole field of the general physical chemistry, he was actively promoting the energetic standpoint as to the conventional thermodynamics [170-181]. Brønsted's suggestions have encountered both positive and negative reactions.

Among the latter ones we may underline the following two [182, 183]. Prof. McDoughall's criticism is excessively harsh, for he explicitly underlines Prof. Brønsted's '*misunderstanding the language of the traditional thermodynamics*' which was definitely going much too far, to our mind. In effect, Prof. McDoughall just wouldn't like to recognize that Prof. Brønsted's aim was in fact a considerable reorientation of this language. Prof. F. H. McDoughall was himself an author of the book entitled '*Thermodynamics and Chemistry*' [184], where he openly states that he is an unequivocal adept of J. W. Gibbs' and M. Planck's formulation of the conventional thermodynamics, so that, to his mind, the latter ought to be well and enough formulated to represent a fully complete branch. Meanwhile, as we have already seen, an indiscriminate adherence to the so-called 'equilibrium thermodynamics' ought to be quite a narrow view of the matter (cf. also [18] and the references therein).

Remarkably, the criticism expressed by H. Højgaard Jensen and E. Krüger [183] sounds anyway much more constructively. E. g., among other sufficiently equitable notes, these authors have found Prof. Brønsted's definition of the 'entropy' notion to be insufficiently clarified – which we are ready to share … Indeed, just as in the J. W. Gibbs' case, Prof. Brønsted had not enough time, due to his natural departure, to our sincere regret…

The latter attitude was shared by the positive reviewers of Prof. Brønsted's contribution to thermodynamics [185-190]. Furthermore, they have also noticed differences between the Energetics of Prof. Brønsted and '*that of Helm, Mach and Ostwald of the decade 1890-1900*'. Besides, the Energetics of Prof. Keenan ought to have its own characteristic features, therefore, it should be of immense interest to try to bring all the 'branches', 'shades' and 'flavors' of the Energetics together, including that of the French school, in striving to formulate the True Thermodynamics… A book by Prof. Dr. K. S. Spiegler [191] could be considered the first fortunate attempt to enter the latter route.

Apart from all the above we would also like to review the fate of the Energetics in the USA. In the field of physical chemistry, there were noticeable efforts to reformulate thermodynamics from the energetics' standpoint [192-197] which had no sensible continuation, to the best of our knowledge... On the other hand, Prof. Dr. Keenan was forcefully trying to combine something quite incompatible: namely, the

energetics based on the rational mechanics on the one hand and on the other – the statistical-mechanical approach according to some powerful approximations (the results by Boltzmann and Gibbs) which weren't (and still aren't, to our regret!) carefully worked through in detail – due to the natural departures of their original authors… This is why, after his first brilliant book [33] and a clear appeal to the physicists [198] his second book came out [199], where the clear thermodynamic thread was lost to some extent (no more tangible formulation of the Second Basic Law, for example)… And such confusions are unfortunately preserved even in the most modern engineering thermodynamics handbooks [200-203], whereas the modern physical-chemical treatises use the term 'Energetics' in some quite different sense [204].

Nevertheless, the energetic standpoint (in the form of the 'exergetic approach') could still overcome all these conceptual difficulties and attracts attention of the numerous specialists all over the world (see [205-214] and the references therein). The '*exergy*' notion logically comes from the ideas of the '*energy availability*', that is, it has to do with the Second Basic Law of thermodynamics, in accordance with the ideas of the thermodynamics' Founders: N. L. S. Carnot, R. Clausius, Lord Kelvin… As we discussed in detail elsewhere [18] (cf. also the above-mentioned formulation of thermodynamic Basic Laws by Prof. Dr. A. F. Horstmann), the rational-mechanical picture of the real thermodynamic processes laws consists in that we are getting the 'livening force, *vis viva*' for them (the force capable of promoting them) – that is, in the energy language, we are getting the most possible amount of kinetic energy from the potential energy, or, in other words, 'from the bank of available energy'. The most perceptible analogy of this 'converting potential energy to a kinetic one' ought to be 'getting a loan of money from your bank'.

As soon as you have the loan, you get some money that is now *available* to you. The next step, is to spend the latter – and what should it be spent for? In our everyday life a lot of things are already organized and prepared – for example, if we wish to get some bread, we just go to a bakery (well, some money might be necessary to spend for refuelling your car - or buying a ticket to use some public traffic – and then you may buy the necessary amount of bread in the bakery for the pertinent amount of the rest of your money).

In principle, this same story takes place during any realistic process requiring some energy costs. Indeed,

the simplest, the ideal case – nothing serves apparently as a block – so the process will go so far, until the energy is available. But normally there are numerous obstacles and hindrances which ought to be overcome, and this definitely requires energy as well. In our example with the available money: The bakery is situated rather far away from your home place. Hence, to buy bread, you need to spend your money not only to pay for the bread as it is, but also to somehow get to the place where your bakery is actually located. Going to bakery and buying something there are thus different happenings which are logically connected to each other – for without getting somehow to bakery we won't be able to buy something there… We might formulate the same story other way: When sitting at home and willing to buy bread at a bakery, we encounter one clear difficulty – or – hindrance – we have to somehow get to the bakery of our choice! This is why we need the money available to us for performing *two* actions – a) to surmount the difficulty and b) to actually carry out our desired task. As soon as the money available to us is enough to accomplish the both mentioned tasks – our mission is successful. But the **_zest_** of this trivial everyday story is:

With respect to buying our bread, our spatial remoteness from the bakery is an obstacle, a hindrance to be overcome on the way to successful accomplishment of the main task – buying our everyday bread. And, in thermodynamic representation of the described event, the *latter* is the *enthalpic* contribution, whereas the *former* is the *entropic* one. And these both ought to compensate each other, for only commensurate events could really be correlated with each other… In our everyday example, the both actions: a) buying bread in a bakery and b) physically reaching the bakery to buy the bread over there – are clearly commensurate and correlated, for the whole story is about *one and the same* object: *THE BAKERY*… Still, for us, 'the users', the main object should in effect be *THE BREAD*, for this is just what we would like to buy – and not the whole bakery… In particular, exactly these deliberations are demonstrating the main difficulty of thermodynamics, as concerns the 'entropy' notion: We ought to be careful, not to confound *what exactly we need to achieve* and the *means to achieve the desired result*… To sum up, **_the 'entropy' is nothing more than the obstacles we need to surmount in order to achieve the desired result_**.

And if we now revert e. g. to systems of biophysical-biochemical interest, that is, to those in the form of

supra-molecular entities consisting of lots of atoms, we recognize that such systems are experiencing numerous diverse dynamical modes which form the physical basis of their functioning. Theoretically, this picture could be successfully and fruitfully studied using the modern computer simulation facilities [49-61]. So, the only essential point here would be – how to adequately interpret the atomic trajectories thus obtained…

Earlier we have already suggested some sophisticated statistical approach based upon the factor analysis [215]. The main point of that approach was to investigate dynamical pair-wise correlations between all the atoms under study. And the factor analysis of correlations allows discovering the factors behind the observed correlations. The latter ought then to be assigned to some realistic intra-molecular processes including great number of atoms… Further on, by consistently applying such an approach, it might be possible to classify some factors, as well as the degree of correlations between the latter, although our computer simulation doesn't deliver any direct approach to study them… On the basis of the observed correlations it should be possible to successfully classify the *enthalpic (energetic)* and the *entropic* factors – that is, *what we would like to achieve* – and *how we would like to achieve the latter*, respectively.

## THE MODERN TRENDS AND CONCLUSIONS

To sum up, even a brief review of the most recent literature devoted to thermodynamics and statistical physics clearly shows that we are currently confronted with a gaily coloured mixture of real concepts and traditional misconceptions – see, for example, the materials of the AIP conference entitled '*QUANTUM LIMITS TO THE SECOND LAW*' [216], as well as the accompanying volume of the journal 'Entropy' containing a number of more detailed reports from that conference [217]. Meanwhile, it is truly inspiring to read serious, thoughtful work trying to overcome the persistent difficulties of the conventional thermodynamics and statistical physics [218-221]. In view of this, an attentive work with elder literature is indispensable: For sometimes we might come to the true treasuries of thoughts and notices, like the books by Prof. Dr. Peter Boas Freuchen (1866-1959) [222, 223]. Who knows, may perhaps reading of these books and conversations with their author was one of the factors led Prof. Dr. Brønsted to his idea of reworking the foundations of thermodynamics… Interestingly, in his thermodynamics book [222] Prof. Freuchen has

devoted a long chapter to the analysis of Prof. Horstmann's results and compared this with the achievements of other authors of that and later time periods…

Bearing in mind all the present discussion, we would first of all like to underline the immense significance of the 'energetic re-consideration' of the (bio)-physical-chemical phenomena, like enzymatic reactions [224] and water properties [225]. As we have already pointed out, the proper theoretical considerations ought to be of crucial importance in this respect. Without going in for the necessary details here (due to the lack of space), we would just like to underline the need of re-considering the interpretation of the relevant computer simulation results, like it was done in [215]. The main point is that to reconcile the gap between the atomistic representation and the Energetics, we ought to be capable of properly analyzing the actual correlations among the atoms in gases, molecules, macro- and supra- molecules. The formal and handy mathematical means for such studies are provided by the so-called '*factor analysis of correlations*' (cf. the corresponding references in [18] and [215]). We are continuing work in this direction…

As we have mentioned mathematics, the insightful work by Prof. Dr. Johann Walter should be mentioned here [226-233]. And – the last, but not the least – when dealing with mathematics, the philosophic aspects should not be forgotten (everything new is actually well-forgotten old) [234, 235].

To conclude our present discussion, we would like to point out that

a) The energetic representation of the conventional macroscopic thermodynamics is the only physically plausible way of dealing with this discipline;

b) There are no more than one unique law of thermodynamics and it is connected with the conservation and transformation of energy, whereas the latter feature is the way to produce driving forces for the relevant processes;

c) As any realistic process experiences ubiquitous hindrances, respectively characteristic for every particular case, for the process to be promoted, its driving force should be enough BOTH to fulfill the requirements of the process itself AND to successfully overcome all the obstacles on the way to the desired result;

d) Thus, the conservation-transformation law is always possessed of its 'opposite side', namely – the imperative to cope with the ubiquitous obstacles;

e) Such a unique law having two opposite sides was the actual suggestion of Nicolas Leonard Sadi Carnot – but, to our sincere regret, it took a considerable time to accept his ingenious idea;

f) The mechanism of a typical physical, chemical, biophysical, biochemical, etc. process consists in activation of the process in question, which triggers all the predestined hindrances as well;

g) The further promotion of the process, the higher the hindrances, so that, to bring the process to its desired outcome, the driving force should be enough to surmount the MAXIMUM POSSIBLE hindrances;

h) This is the genuine logics of the notorious and unavoidable 'entropy increase': the more 'pretensions' has the process, the more obstacles should it overcome;

i) Within thermodynamics, it is very convenient and straightforward to describe the latter situation in terms of the 'Enthalpy – Entropy Compensation' (EEC);

j) At the lower levels of organization – mesoscopic, nanoscopic, microscopic – the physical laws remain the same as at the already discussed macroscopic one;

k) To produce a universally valid picture for all the possible levels, one ought to guarantee the relevant interpretation of the microscopic dynamics' trends;

l) On the other hand, statistical physics ought to be reformulated to avoid operating with the fuzzy notion of the "large number of molecules";

m) Finally, the pertinent mathematics to describe the 'EEC' is the differential games theory;

## ACKNOWLEDGEMENT

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